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Preliminary communication

PERETHYLCYCLOPOLYSILANES: $(Et_2Si)_4$ THROUGH $(Et_2Si)_8$

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Summary

Preparation and characterization by UV spectroscopy, chromatography, mass spectrometry and elemental analysis of perethylcyclopolysilanes, $(Et_2Si)_n$, (n = 5—8), is described. The compounds with n = 5 and 7 are the major products while the n = 6 compound is the most stable in the $(Me_2Si)_n$ series.

Despite the interest shown in cyclic polysilanes arising from their property of electron delocalization [1], except for the permethyl compounds [2] only a few alkyl substituted rings are known [1,3]. We now report the preparation and initial characterization of the perethylcyclopolysilanes $(Et_2Si)_n$, where n = 5, 6, 7 and 8.

It has previously been claimed that condensation of diethyldichlorosilane (Et_2SiCl_2) with Li produces $(Et_2Si)_6$ [4]. We find that $(Et_2Si)_6$ is indeed formed in this reaction, but only in small yield. The main products are instead $(Et_2Si)_5$ and $(Et_2Si)_7$, along with lesser amounts of $(Et_2Si)_8$ and $(Et_2Si)_6$. In a typical reaction, 600 ml of dry THF and 2.78 g (0.4 mol) of Li wire were placed in a 1-l flask equipped with a stirrer and a N_2 inlet. Et_2SiCl_2 (31.4 g, 0.2 mol) was added dropwise with stirring over 3 h while the temperature was maintained at 0°C. Stirring was continued for 20.5 h at 0°C, after which the solution was filtered to remove any unreacted Li. Hexane was then added, and the solution was washed with water, dried, concentrated, and passed through a short alumina column. The solvent was then evaporated to give 15.5 g of a white, waxy solid consisting of the cyclopolysilanes as well as numerous volatile species, many of which appear to be siloxanes. GLC analysis showed the yield of ring compounds to be 14% $(Et_2Si)_5$, 4% $(Et_2Si)_6$, 41% $(Et_2Si)_7$ and 8% $(Et_2Si)_8$.

If the Et_2SiCl_2 condensation is carried out with a 10% excess of potassium metal, $(Et_2Si)_5$ is obtained in 91% yield but only traces of higher rings are formed. When lithium metal is used in 10% excess, the higher rings are partially converted to $(Et_2Si)_5$. These results lead us to conclude that, although $(Me_2Si)_6$ is the most stable oligomer in the $(Me_2Si)_n$ series [5], the thermodynamically favored product in the $(Et_2Si)_n$ series is the five-membered ring compound.

Rings larger than $(Et_2Si)_5$ are evidently kinetic products. By comparison, the reaction of one equivalent of Li with Me_2SiCl_2 at 0°C gives $(Me_2Si)_6$ and $(Me_2Si)_8$ as the principal cyclic products [6].

The perethylcyclopolysilanes are readily obtained pure by HPLC*. The six-, seven-, and eight-membered rings are colorless crystals, while $(Et_2Si)_5$ is obtained as a clear, greasy solid. All are indefinitely air-stable. These compounds were identified by peak matching using a high resolution mass spectrometer and by elemental analysis. ^{1}H NMR reveals a multiplet for each in the δ 0.8—1.2 region. The UV λ_{max} in 2,2,4-trimethylpentane are given in Table 1. These polysilanes melt over broad temperature ranges and appear to undergo phase transitions at temperatures well below their melting points, in a manner similar to the $(Me_2Si)_n$ oligomers [7].

TABLE 1

UV SPECTRA OF $(Et_2Si)_n$, n = 5—8

n	λ_{max}
5	266^a(1100), 255(sh)(11000), 210(sh)(30000)
6	259(sh)(1900), 237(5800), 205(sh)(160,000)
7	257(sh)(4400), 244(1400), 227(sh)(18000), 200(sh)(60000)
8	~260(sh)(6100), 244(21000), 221(sh)(24000), 196(sh)(82000)

[a] Probable doublet.

Irradiation of the perethylcyclopolysilanes results in the elimination of diethylsilylene, Et_2Si. For example, photolysis of $(Et_2Si)_7$ in cyclohexane at 254 nm for 15 min produces 22% $(Et_2Si)_6$ and 32% $(Et_2Si)_5$, as well as 14% of a new compound, shown by GC-MS to be $(Et_2Si)_4$. The ring contractions evidently occur by the sequence $(Et_2Si)_n \xrightarrow{h\nu} (Et_2Si)_{n-1} + Et_2Si$: for n = 7, 6 and 5. The presence of the silylene was confirmed by trapping with Et_3SiH to give high yields of the insertion product, Et_3SiEt_2SiH, which was identified by GC-MS. This reaction provides a useful route to $(Et_2Si)_6$ and $(Et_2Si)_4$, which are not available in large yield from the lithium condensation reaction.

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*Separations were carried out using MeOH/THF on a Whatman M-9 column containing Partisil-10 ODS.